COMPARATIVE ANALYSIS OF STRUCTURE FORMATION IN THE THIN FILMS OF SOLID ELECTRODE MATERIALS PRODUCED BY DIFFERENT METHODS

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At present to produce the thin films of solid electrolytes for lithium secondary battery the methods of vacuum thermal, electron-beam and magnetron radio-frequency and electron-spraying are mainly used.

In this work the results of X-ray diffraction (XRD), optical and electron-microscopic analysis of the glassy material films of Li_2O-Li_2SO_4-B_2O_3 system deposited by the above methods on a stainless steel substrate are presented.

Vacuum thermal spraying allowed to produce rather thick (upto 10µm) films with amorphous-crystalline structure. Crystalline phase according to XRD analysis has a stoichiometric formula $Li_4B_{10}O_{17}$, however, at microscopic investigation it is not observed, with the exception of a small (less 1%) quantity as the grained formations (Fig.1).Computer check of substrate temperature, vapor density, temperature conditions of evaporator provides for the good indicator of thickness variation (less 5%) at 5-6 µm/sec spraying rate.

Electron-beam spraying in a graphite crucible is as efficient as vacuum thermal one, however, the films contain far more the crystalline phase with a coarse needlelike structure (Fig.2). Besides, non-controlled carrying away of the material was observed during the initial period of spraying as a result of the electrostatic effects of interaction between a target and electron beam effecting negatively on the film variation in thickness, which has reached 30%.

At magnetron spraying the targets manufactured by the application of the thin layer of flashed powder of the material on the conducting substrate were used. The target preparation was carried out in atmosphere of high purity flowing argon with ultrasonic stirring of melt to prevent the possible liquation effects. The material deposition rate at spraying was 0.1µm/h. Thus, the films with X-ray amorphous structure and a thickness not more than 0.5µm, have been produced. Electron microscopic analysis (Fig.3) has not exposed any structural elements on a film surface.

Determination of the ion conductivity by impedance method results in the following values for the samples produced by the different methods:

- vacuum thermal – $6.2 \bullet 10^{-4}$ S•cm^{-1}
- electron-beam - $6.0 \bullet 10^{-5}$ S•cm^{-1}
- magnetron - $2.1 \bullet 10^{-4}$ S•cm^{-1}

Fig.1. Film structure of Li_2O-Li_2SO_4-B_2O_3 system produced by vacuum thermal spraying method, x500

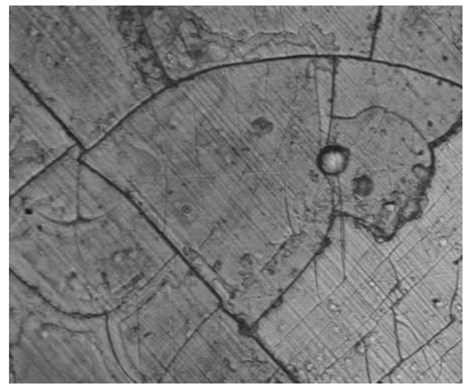


Fig.2. Film structure of Li_2O-Li_2SO_4-B_2O_3 system produced by the method of electron-beam spraying, x100

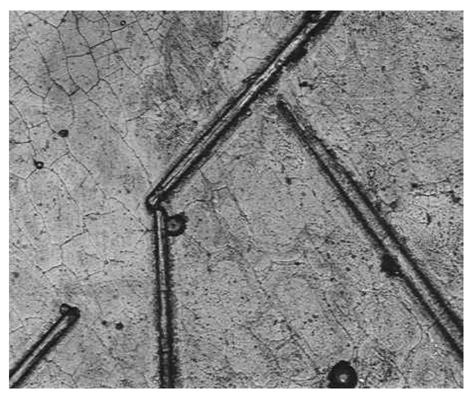
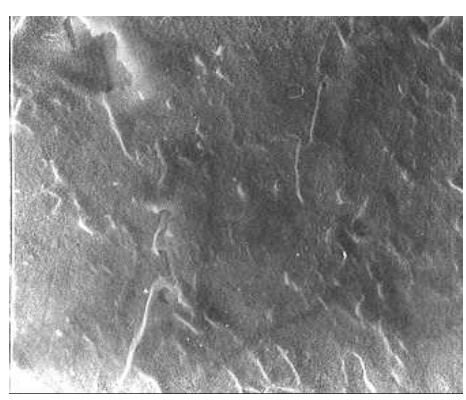


Fig.3. Film structure of Li_2O-Li_2SO_4-B_2O_3 system produced by the method of magnetron spraying



method, x3000 (SEM).